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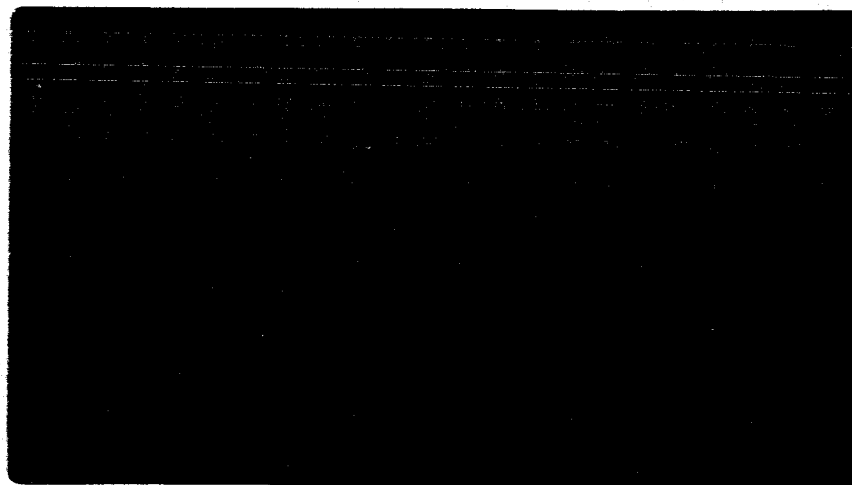
Technology Center   Chicago 16, Illinois

Report No. IITRI-C6014-4
(Triannual Report) a_g 47

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/
EMITTANCE RATIOS)

George C. Marshall Space Flight Center

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DEVELOPMENT OF SPACE–STABLE THERMAL–CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/EMITTANCE RATIOS)

May 20, 1963 through September 20, 1963

(NASA Contract No. NAS8-5479;
IITRI Project C6014)

Prepared by

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Huntsville, Alabama

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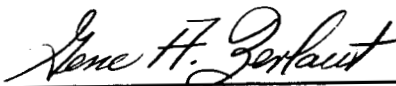
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FOREWORD

This is Report No. IITRI-C6014-4 (Triannual Report) of Project C6014, Contract No. NAS8-5479, entitled "Investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles". The report covers the period from May 20, 1963, to September 20, 1963.

Major contributors to the program included Gene A. Zerlaut, Project Leader; Y. Harada and J. Miller, inorganic coatings; Edward H. Tompkins and Dr. Klaus Guenther, microporous structures; Warren Jamison, space-chamber operation; O. H. Olson, optical measurements; and Douglas G. Vance, silicone paint preparation.
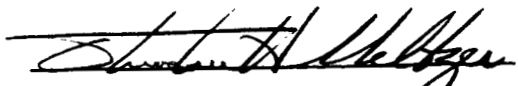
Data are recorded in IITRI Logbooks C13423, C13736, C13802, and C14176.

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Respectfully submitted,

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ABSTRACT

A

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS
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Investigations were conducted to decrease the solar absorptance
of zinc oxide-pigmented potassium silicate and methyl-silicone
paints by employing techniques to (1) increase their ultraviolet
reflectance without expense to their stability, and (2) maximize
their reflectance in the visible and near-infrared portion of the
solar spectrum.

Attempts to increase the ultraviolet reflectance of zinc oxide
systems involved the creation of microporous structures in the
paint vehicles to enhance the scatter of ultraviolet light. These
attempts have been confined to developing microbubbles in polymer
films and have resulted in microporous films which show good
scattering characteristics in the ultraviolet region. Another
technique involved the use of dual-coat systems comprising a zinc
oxide first coat and a very thin, ultraviolet-reflecting tin oxide-
pigmented topcoat. These experiments were unsatisfactory since
the topcoat did not appreciably increase the ultraviolet reflectance
of the system although it did decrease the reflectance in the
visible and near-infrared regions.

Also discussed are the reflectance and solar absorptance of
various compacted zinc oxide powders, preliminary investigations of
the microstructure of the potassium silicate paints, the effect of
"tumbling" a zinc oxide-silicate specimen in an Alconox-water mixture,
and the effect of pigment volume concentration on the spectral
reflectance of zinc oxide-pigmented methyl silicone elastomer paints.

IIT RESEARCH INSTITUTE   AUTHOR

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS (PAINTS WITH LOW SOLAR ABSORPTANCE/EMITTANCE RATIOS)

I. INTRODUCTION

The problems associated with the choice of surfaces and surface coatings for the passive thermal control of spacecraft have received considerable attention in the past five years. The greatest portion of these investigations have involved the evaluation of the stability of potentially useful coatings in laboratory simulated space (ultraviolet) environments. These coatings--particularly the organic coatings--have often been commercial formulations or experimental formulations which are not designed for maximum reflection of solar energy. However, as spacecraft become larger and more complex, the requirement for highly efficient solar reflectors and flat reflectors becomes more and more urgent. Efficient solar reflectors are needed both for radiator surfaces and on tankage designed for the orbital storage of cryogenic propellants.

Until recently, the lack of available inorganic and organic pigment binders (or vehicles) which are sufficiently resistant to ultraviolet irradiation in vacuum has prevented the effective maximization of solar reflectance. However, recent studies at IIT Research Institute (ref. 1) have shown that the inorganic alkali silicates and the semiorganic methyl silicone polymers are exceptionally stable to ultraviolet radiation in vacuum when pigmented with zinc oxide. Sibert (ref. 2) and more recently

Gilligan, Sibert and Greening (ref. 3) have also shown that the
inorganic alkali silicate paints--namely, sodium silicate--are
relatively stable to ultraviolet radiation in vacuum, and they
have described the effects of space simulation on potassium
silicate pigmented with zircon, calcium silicate, and lithium
aluminum silicate.

In general, the alkali silicates pigmented with ultraviolet-
reflecting pigments such as alumina, zircon, or calcium silicate
are somewhat less stable than alkali silicates pigmented with
zinc oxide (ref. 1, 4). Unfortunately, however, the solar
absorptances of zinc oxide-silicate paints are not as low as
those of the paints based upon lithium aluminum silicate, zircon,
and calcium silicate. Zinc oxide-potassium silicate paints have
been prepared with solar absorptance values as low as 0.14, but
the values are usually in the range 0.15 to 0.17 (ref. 1, 4).
Lithium aluminum silicate and zircon paints have been prepared with
solar absorptances of 0.10 and 0.12, respectively, which reportedly
degrade to respective values of 0.14 and 0.18 in 600 equivalent
sun-hours (ESH) exposure (ref. 3). Therefore, one would like
the reflectance characteristics of systems such as zircon   or
lithium aluminum silicate paint combined with the stability of
the zinc oxide system, which has been shown to degrade from 0.16
to only 0.18 in over 4000 ESH of ultraviolet radiation in
vacuum (ref. 1).

The ultraviolet and visible absorption spectra of zinc
oxide are well known. The reflectance of zinc oxide paints begins

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II. MICROBUBBLE STRUCTURE IN PAINT VEHICLES

The objective of this phase was to produce white coatings with bubbles small enough to scatter ultraviolet light effectively in vehicles of high solar stability. The formation of bubbles in a suitable vehicle can be achieved by mechanical, physical, and chemical methods. These methods have the common step of bringing the composition to be "foamed" into a liquid or plastic state within specified viscosity limits. The formation of bubbles is achieved by the use of foaming agents. In this instance the term foaming agent denotes any material-solid, liquid, or gaseous-or any combination of materials capable of producing a bubble structure.

A. Experimental Methods

1. Mechanical Methods

Bubbles can be obtained in a suitable plastic; vigorous agitation of an emulsion, a suspension, or a solution of the resin produces a froth which is then gelled and fused or cured. Originally developed for producing latex foam, this method has been adapted to foaming polyvinyl acetal, polyvinyl chloride plastisols, and urea-formaldehyde resins. This method has not yet been used to produce a bubble structure in silicone resins.

2. Physical Methods

Physical methods use materials as bubble-forming agents that change their physical state during the foaming operation, e.g., compressed gases, volatile liquids, or soluble solids.

Although the physical foaming processes use inexpensive foaming agents, they require rather costly equipment designed specifically for a given application. We tried to avoid such equipment by applying methods which were relatively simple but effective. The foaming agents can be chosen from odorless, nontoxic, and non-corrosive substances. They have no residue, and therefore, have no adverse effect on the physical and chemical properties of the resulting foam; this is particularly important for the preparation of ultraviolet stable coatings. Elemental gases, nitrogen in particular, have been proposed as foaming agents in several foaming processes which use specially deisgned extruders. In these processes, the molten plastic, e.g., polyethylene, is impregnated with nitrogen, and expansion occurs when the plastic material leaves the orifice of the extrusion die.

Another way of obtaining a bubble structure is by dissolving in the polymer, under pressure, normally gaseous agents, such as methyl chloride, propylene, or dichlorodifluoromethane. Similar foaming techniques utilize the rapid evaporation of volatile liquids, such as diisopropylether or even water. Our best results were obtained with a solution of a silicone resin (plus catalyst) in methylene chloride or Freon 11 (trichloromonofluoromethane) which was sprayed with an airbrush on a heated plate. By this means bubble formation in the resin layer occurred through the sudden evaporation of the organic solvent and the trapping of air bubbles in the rapidily curing resin.

3. Chemical Methods

In chemical bubble formation, the expanding gas is generated in situ, i.e., within the matrix of the polymer. The cell-forming gas can be produced as a by-product of a chain extension or cross-linking of the polymer, e.g., the formation of polyurethane foams with carbon dioxide liberated from the reaction between carboxyl-bearing alkyd resins and an isocyanate. Similarly, the condensation of phenol and formaldehyde produces water as a by-product which , in the form of steam, is capable of foaming the resulting phenolic resin. The expanding gas can also be developed in a reaction between a resin hardener, e.g., an acid, and an additive such as sodium becarbonate or metal powder. Still another chemical foaming method relies on heat-sensitive additives (chemical blowing agents) as sources of the expanding gas.

Chemical blowing agents, frequently called foaming agents in the plastics industry, are inorganic or organic materials that decompose under the influence of heat to yield at least one gaseous decomposition product. The most characteristic property of chemical foaming agents is the temperature at which the gas is liberated. In fact, the decomposition temperature determines the usefulness of a foaming agent in a given plastic material and also governs the conditions under which the foamable compound is to be processed. Since we are relying only on certain silicone resins with specific curing properties, the selection of a suitable blowing agent is especially critical. The range of potential blowing agents extends from baking powder to explosives. Indeed,

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in the past 40 years at least a thousand different products have been proposed as chemical foaming agents. The compounds which we selected for our investigations are listed together with their trade name and decomposition temperature in air in Table 1.

Table 1

CHEMICAL BLOWING AGENTS

Compound	Trade Name	Decomposition Temperature in air, °C
Ammonium carbonate	–	60
Ammonium nitrite	–	70
Hydrazine hydrate	–	200
Azobisformamide	Kempore	195-200
	Celogen AZ	195-200
Diazoaminobenzene	DAB	103
n,n'-Dimethyl-n,n'-dinitroso-terephthalamide	Nitrosan	105
4,4'-Oxybis(benzenesulfonyl-hydrazide)	Celogen OT	150
p-Diazo-n-ethyl-n-benzyl-aniline zinc chloride	(Experimental)	–

B. Experiments with Selected Compounds

1. Kalfax

Preliminary results show that we have to make up our own version of Kalfax for application in this program. Kalfax film, which has a diazo compound that is photolyzed to nitrogen gas in ultraviolet radiation is too thermoplastic, and there is too much visible color after the diazo compound decomposes. We found similar results when we photolyzed p-diazo-N-ethyl-N-benzylaniline zinc chloride in polyvinylpyrrolidene. The decomposition products had a deep brown color. The color problem may be insurmountable, but after a patent search is completed we shall make some of our own films and try generating the nitrogen bubbles.

2. Polyvinylpyrrolidene (PVP)

A 25% aqueous solution of PVP with up to 20% ammonium nitrite was one of the first compositions tried. In a series of experiments it was found that an aqueous solution of 25% PVP and 4% ammonium nitrite gave the best results. This mixture was applied to a glass slide and dried at approximately 55°C. Afterwards the clear film was heated with a hot-air stream, and a bubble layer developed. PVP is not stable in ultraviolet radiation, but these experiments gave us some experience with water-base systems.

3. Sodium Silicate Solution (SSS)

Commercially available sodium silicate solution (SSS), 40-42°Be, was used. Mixtures of SSS and 85% hydrazine hydrate solution covered a range of concentration up to 500 g N_2H_4 H_2O/liter.

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To catalyze the decomposition of hydrazine, which is stable up to 200°C, dilute solutions of palladium and mercury salts were added. However, the resulting bubbles were too large.

The use of ammonium nitrite or ammonium carbonate in combination with SSS was not successful because of the decomposition of the ammonium salts due to the strong alkalinity of SSS.

Nitrosan did not seem to interact with SSS, but it was not soluble in SSS. Experiments were performed to disperse Nitrosan in SSS by ball-milling. However, even a milling time of 48 hrs did not give small enough Nitrosan particles.

4. LTV-602

LTV-602, a clear methyl-silicone potting compound, requires a catalyst for curing. An emulsion of LTV-602, hydrazine solution, and catalyst was heated to 100°C; mixtures of LTV-602 with solid ammonium carbonate (approximately 20% ammonium carbonate) were also tried. Mixtures which were ball-milled or prepared without ball-milling showed similar behavior. It was not possible to prepare a fine dispersion of ammonium carbonate in LTV-602. Therefore, the resulting bubbles were of different sizes and too large.

Mixtures of LTV-602 with Kempore 125 (up to approximately 13% Kempore 125) were ball-milled, and benzene was added to decrease the viscosity. After the solvent was removed by evaporation, a catalyst was added, and the resin was cured.

Different concentration ratios of LTV-602:Kempore 125 were tried, and the cured and uncured samples were heated to various

temperatures up to 250°C. Zinc chloride was added in order to catalyze decomposition of the Kempore. The results were negative since the blowing agent, Kempore, appeared to be very stable under the experimental conditions.

Because Kempore is insoluble in the common solvents, it was not possible to prepare a homogeneous solution of this agent in LTV-602. Kempore is soluble in dimethylsulfoxide, but LTV-602 was insoluble in this solvent.

Better results were obtained with Nitrosan. Nitrosan is soluble in common organic solvents. Solutions of up to 5% Nitrosan in LTV-602 were prepared by using toluene or methylene chloride as the solvent. After evaporation of the solvent, the Nitrosan was incorporated in the solid layers of resin. However, the relatively large crystals of Nitrosan gave large bubbles of nitrogen during the decomposition of the agent. A solution of the silicone resin and Nitrosan in methylene chloride was sprayed on a heated slide. Since the temperature of the glass slide was about 50°C, the solvent evaporated immediately and no growth of the original small Nitrosan crystals could occur. In the subsequent operation, the incorporated Nitrosan crystals were decomposed at elevated temperatures. However, satisfying results were not obtained since the viscosity of the silicone resin at the decomposition temperature of the Nitrosan is critical for the formation of the desired small bubble size and these parameters are unfavorable in the case of the resin LTV-602.

5. Silicones SR 80 and SR 53 (General Electric)

Both silicone resins are solutions in toluene and are air-drying, i.e., they do not need the addition of a catalyst for curing. Ball-milling of mixtures of silicone resins (plus toluene) with Nitrosan did not give the desired small particle size of Nitrosan; generated bubbles were too large. Better results were expected by spraying mixtures of silicone resin and Nitrosan dissolved in methylene chloride. However, the ratio of the viscosity of the resin to the decomposition temperature of Nitrosan was again unfavorable, thus good results were not obtained.

6. Silicone Resin 806A (Dow Corning Corporation)

The experiments performed with silicone resin 806A gave similar results to those described for General Electric's SR30 and SR53 resins. Resin 806A is a phenyl-methyl silicone resin. When solutions of the resin in methylene chloride (1:1) were applied to glass slides and cold air was blown over the layer, a "blushing" effect was noticed; this resulted from the rapid evaporation of the solvent and partial condensation of water from the atmosphere on the resin layer. However, this effect changed only the surface of the layer; no bubbles were formed in the interior of the resin. Spraying of the solution of the resin in methylene chloride with an airbrush gave better results. But the bubbles formed were still too large and the resin layer was still highly translucent.

7. Silicone Resin R-5

Resin R-5 is an experimental methyl-silicone resin prepared in our laboratories. It is one of the most ultraviolet-resistant

paint vehicles available on irradiation in vacuum (ref. 1). It can be made to air-dry by the addition of tetrabutoxy titanium (TBT) which acts as a cross-linking or gelling agent. However, TBT-gelled silicone resins still require heat to fully cure. Resin R-5 may be cured by the addition of zinc octoate or diethylenetriamine catalysts. Variations of the resin:TBT or catalyst ratio affect the curing properties of the resin considerably. This behavior is important for our objective of trapping gas bubbles inside the resin layer. So far experiments have been performed with solutions of the resin and TBT in methylene chloride, Freon 11, and Freon 112. Experiments with higher-boiling solvents, such as Freon 112, toluene, etc., have been generally unsuccessful. The flushing effect mentioned above was again observed when methylene chloride or Freon 11 were used as solvents. Micrographs showed that the bubble size at the surface of the cured resin layer was in the micron range. However, since the bubble formation took place only on the surface of the resin layer, the layer was partially translucent and unsatisfactory for our application. Spraying a solution of the resin and TBT in methylene chloride with an air brush on a heated glass plate gave considerably better results. A 30% (by volume) solution of the resin in methylene chloride and a 10% (by volume) solution of TBT in methylene chloride were used. Best results were obtained by spraying a 1:1 mixture of both solutions on glass slides which had a temperature of approximately 150°C. A white, slightly translucent resin layer was obtained, it showed a definite bubble

structure under the microscope. Although the bubbles were still larger than desired for optimum performance, the ultraviolet reflectance of this resin layer was relatively high (Figure 1). The three curves represent the reflectance of the resin layer as a function of wavelength against a black backing (curve I), an aluminum backing (curve II), and a magnesium carbonate block backing (curve III). The measurements were made against a magnesium carbonate standard. The dependance of reflectance on the backing shows that the sample was transparent. However, even with a black backing the layer exhibited a constant reflectance down to 3600 A. Incorporation of more and smaller bubbles in the resin layer will reduce its transparency and increase the reflectance. All three curves coincide at approximately 3250A; this is attributed to the size of the bubbles which may be too large to efficiently scatter light of shorter wavelengths.

These results demonstrate that bubbles incorporated into a suitable matrix are very effective for scattering in the visible and near-ultraviolet regions.
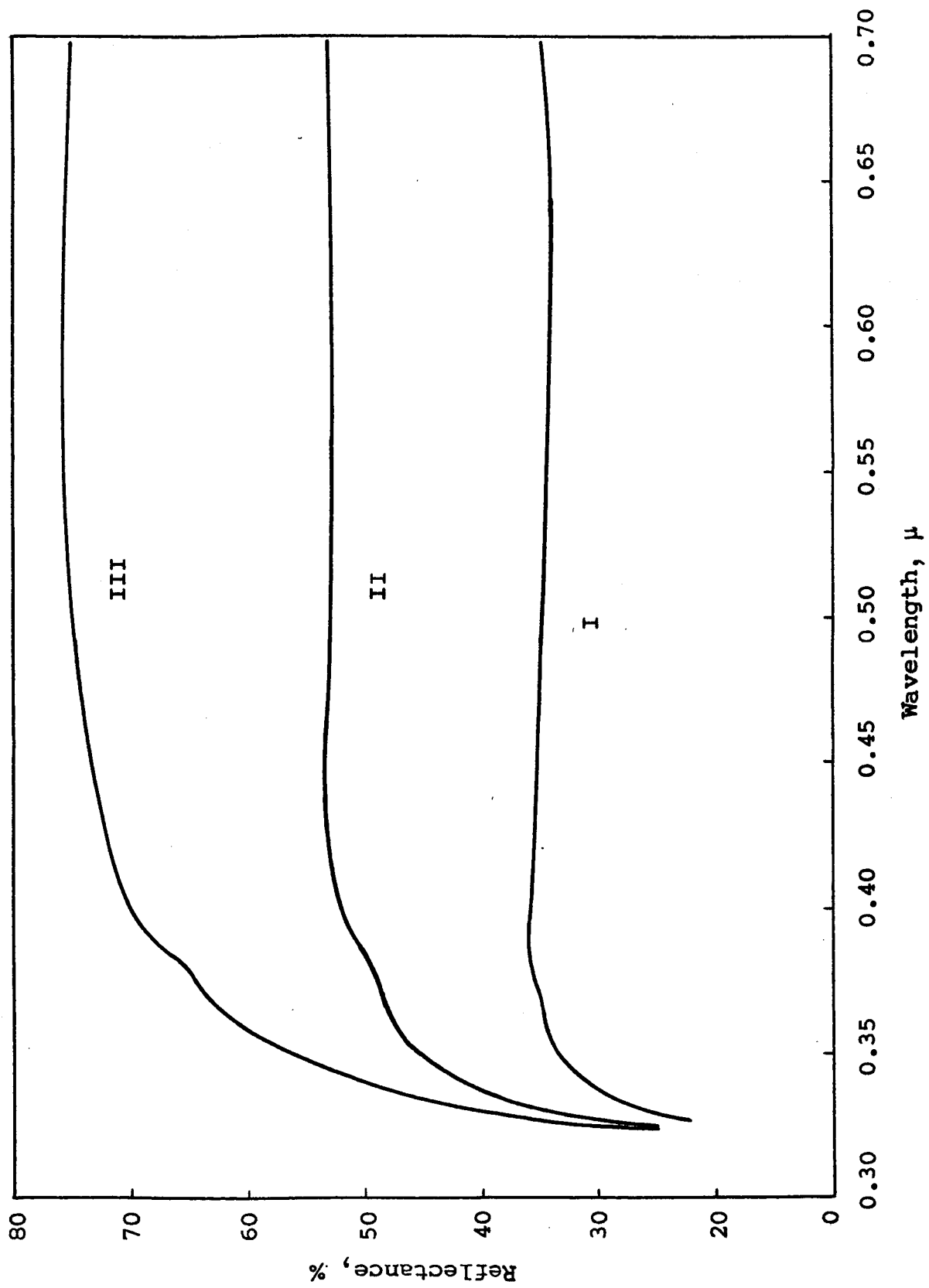
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Figure 1

REFLECTANCE OF FOAMED SILICONE R-5

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III. INORGANIC COATINGS

The initial work with inorganic coatings was primarily concerned with lowering the solar absorptance of the zinc oxide-potassium silicate system. This coating composition was found to be the most stable to ultraviolet irradiation in vacuum of all the systems examined in a program for the Jet Propulsion Laboratory (ref. 1). A limiting solar absorptance for zinc oxide of about 0.13 is observed due mainly to its strong ultraviolet absorptance. Increasing the reflectance both in the near-ultraviolet region and also in the infrared portion of the spectrum is necessary for attaining lower solar absorptance.

An investigation of the optical characteristics of various zinc oxide powders as functions of particle size and manufacturer was conducted. The reflectances of a number of commerical zinc oxide powders were measured. Sample preparation consists in pouring the powder into a copper ring placed on a vellum-covered steel plate. A steel disc of 1-1/2 inch diameter (equal to the inside diameter of the ring) is fitted into the ring covering the pigment. A pressure of 5,000 psi applied on the steel disc results in a specimen with one exposed face for reflectance determination. No binders or lubricants were used, thus averting the possible effects of foreign materials.

Information concerning the physical properties of the various powders as well as solar absorptance values are presented in Table 2. Absorptance values are reported as α_1 and α_2 where

$$\alpha = \alpha_1 + \alpha_2$$

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Table 2

PROPERTIES OF ZINC OXIDE POWDERS

Manufacturers Designation	Manufacturer	Purity, %	Mean Particle Size, μ	Remarks	Solar Absorptance		
					α_1	α_2	α
AZO-88	American Zinc Sales	99.20	0.90		.145	.075	.219
AZO-77	American Zinc Sales	99.80	0.14		.093	.070	.163
AZO-66	American Zinc Sales	99.80	0.20		.086	.050	.136
AZO-33	American Zinc Sales	99.20	ca. 0.40	Acicular	.106	.073	.179
SP 500	New Jersey Zinc	>99.90	0.25-0.35	Spectrographic grade	.092	.037	.128
SP 500	New Jersey Zinc	>99.90		Calcined: 700°C/16 hr	.091	.037	.128
SP 500	New Jersey Zinc	>99.90		Calcined: 700°C/112 hr	.096	.037	.133
SP 500	New Jersey Zinc	>99.90		Calcined: 1000°C/1 hr	.116	.043	.159
SP 500*	New Jersey Zinc	>99.90	2.1 (initial)	Calcined: 700°C/40 hr	.116	.041	.157
USP 12	New Jersey Zinc	99.80	0.30		.089	.046	.136
XX 254	New Jersey Zinc	99.60	1.5		.114	.056	.170
E-P 730	Eagle-Picher	99.50	5.4		.164	.085	.249

*Large particle size, 2.1 μ, SP 500 supplied by the manufacturer.

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α_1 corresponds to that half of the sun's energy spectrum which lies below 0.7 μ wavelength, and α_2 corresponds to that half which lies above 0.7 μ. Splitting α into components offers two advantages: departure from "whiteness" is immediately apparent from α_1, and easier comparison can be made between powders.

Spectral reflectance curves are graphically illustrated in Figure 2, 3, and 4. Among the "AZO" series shown in Figure 2, lowest solar absorptance is exhibited by AZO-66. Although the reflectance of AZO-77 approaches that of AZO-66 in the visible portion of the spectrum, a rapid reflectance drop-off in the infrared since AZO-77 contributes to a higher solar absorptance. The larger particle-sized AZO-88 displayed a higher irradiation reflectance, but its poor reflectance in the visible caused a relatively high solar absorptance.

Spectrographic grade SP 500 possessed the lowest solar absorptance among the commerical zinc oxides. AZO-66 is more reflective in the visible region, i.e., 0.38-0.70 μ, than SP 500, whereas AZO-77 possesses about the same reflectance as SP 500 in this region. This high purity material manifests its superior reflectance in the infrared wavelength region. As tabulated in Table 2, α_2 of SP 500, .037, is considerably less than that of AZO-66, .050, or AZO-77, .070. Calcination of SP 500 at 700°C did not significantly affect the solar absorptance. However, a higher temperature, 1000°C, causes a distinct reflectance loss in the visible. Use of a calcined, larger particle size SP 500, 2.1 μ, results in lowered visible reflectance and slight upgrading at
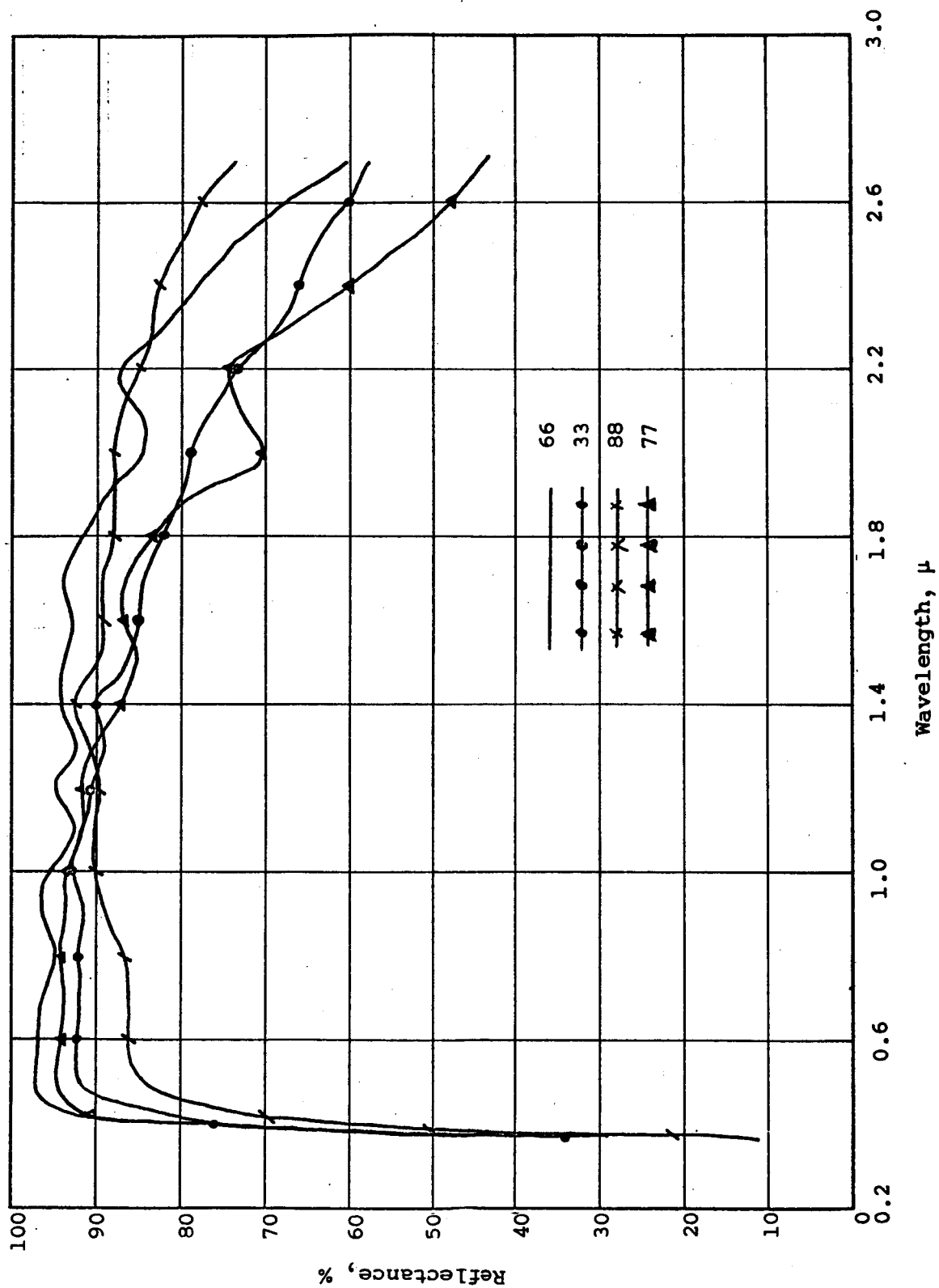
Wavelength, μ
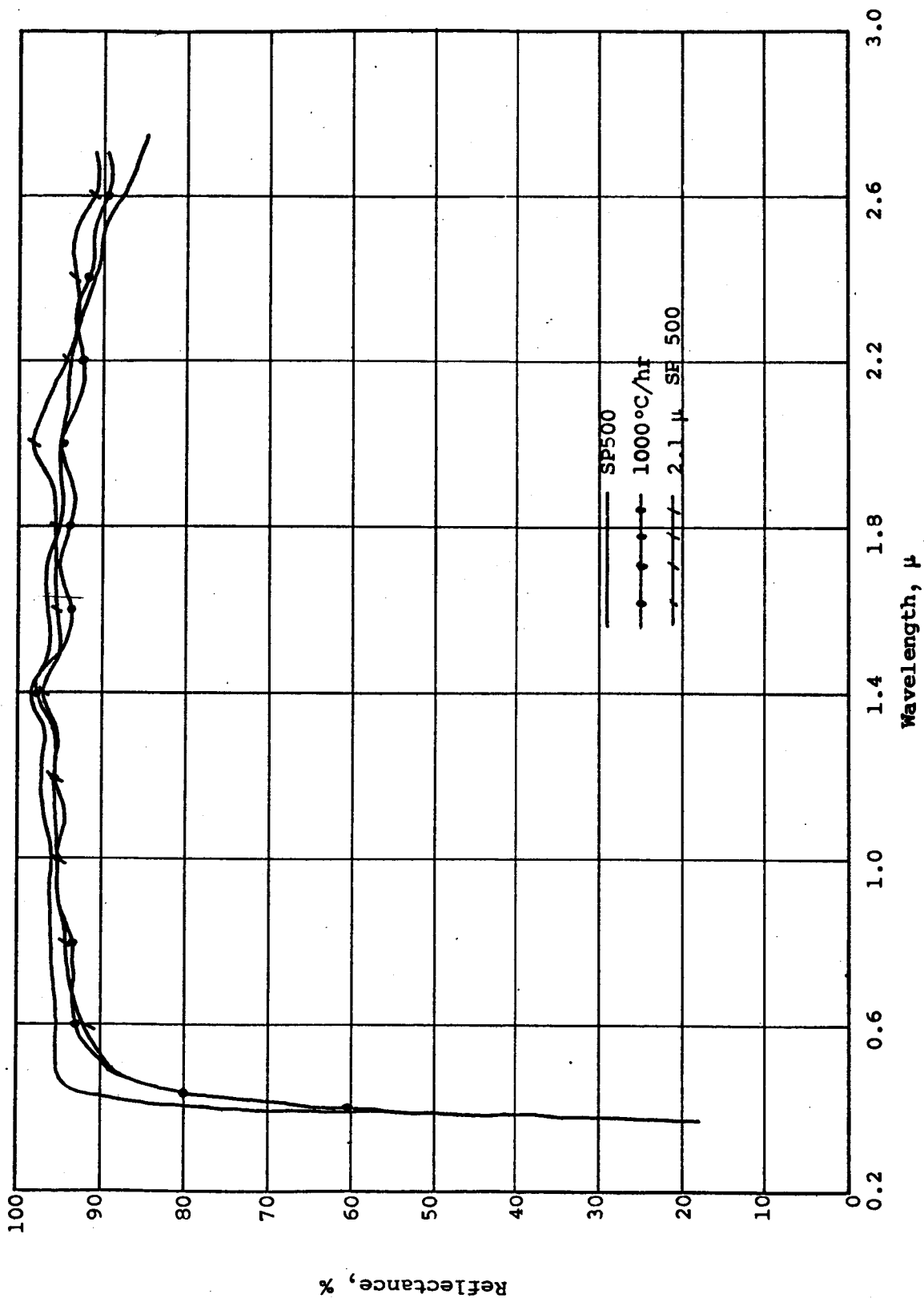
Figure 2

SPECTRAL REFLECTANCE CURVES FOR AZO ZINC OXIDE POWDERS

Figure 3

SPECTRAL REFLECTANCE CURVES FOR SP 500 ZINC OXIDE POWDERS

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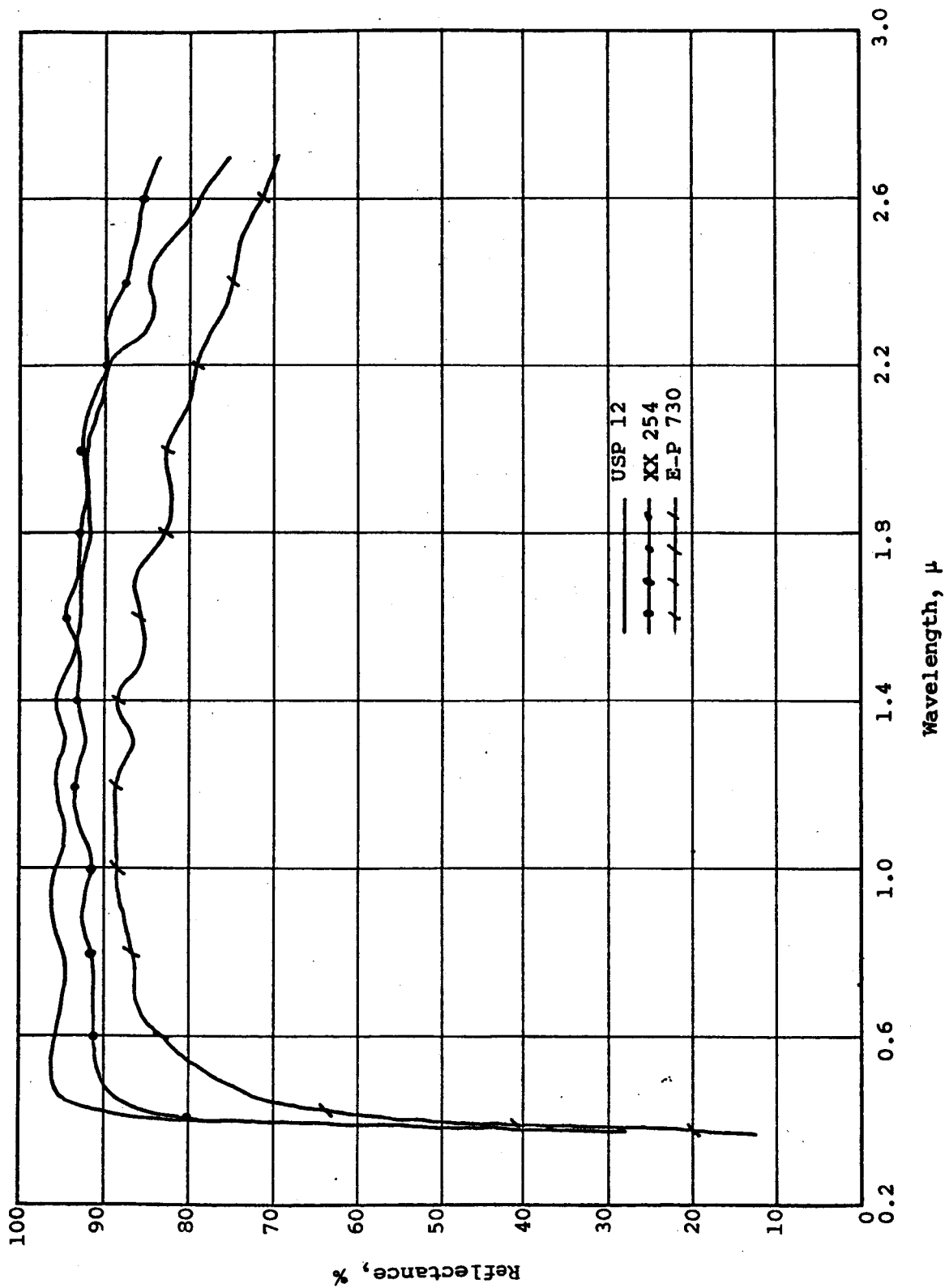
Wavelength, μ

Figure 4

SPECTRAL REFLECTANCE CURVES FOR MISCELLANEOUS ZINC OXIDE POWDERS

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wavelengths greater than 2.0 μ. Curves for these powders appear
in Figure 3. Not illustrated are the 700°C calcined SP 500 materials
which display curves practically identical to the uncalcined powder.

Figure 4 illustrates the spectral reflectance of USP 12
which also has a relatively low solar absorptance and of two
materials of larger particle size, XX254 and E-P 730. The Eagle-
Picher material was visually yellow and had the highest solar abso
absorptance of the zinc oxides studied.

These studies indicate that reflectance at the longer
wavelength is improved with the use of larger particles, which
is consistent with light-scattering theories. However, half of
the solar flux is concentrated in the part of the spectrum
below 0.7 μ and in this region the reflectance must be upgraded.
For example, for the SP 500 powders, the ratio of the energy
absorbed below 0.7 μ to that above, ranges from 2.5 to 2.8:1. This
is primarily due to the characteristic strong absorption of zinc
oxide below 0.4 μ.

A study is being made of the effects of microstructure on
reflectance for zinc oxide-potassium silicate coatings. In a
composite coating the supporting network will influence the
reflectance by providing a second phase as well as by altering
the closeness of particle packing and the size and distribution
of voids.

Glass slides have been sprayed with several different paint
formulations and examined under a microscope. The zinc oxide
pigments used were: Eagle-Picher 730, New Jersey Zinc SP 500,

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American Zinc Sales AZO-88, American Zinc Sales AZO-77; the binder was PS7; the vehicle was water. The solids ratios with each pigment were varied, and the pigment/binder ratio was kept the same, 4.30:1. The glass slides are convenient for examining both the initial and final coating layers (the glass-coating interface and the coating-air interface).

Attempts have been made to improve microscopic coating examinations by adding dyes to the mixed paints before spraying. This procedure is advantageous only when large amounts of dye are added. At this time a preferable method is to spot-dye the coatings after it is sprayed and dried. This technique cannot be used on some coatings which have a high solids content.

Distinct differences have been observed in the networks obtained with the above mentioned grades and sizes of zinc oxide. Preliminary investigations have disclosed the following:

(a) SP 500: solids ratios of 46.3 to 56.9%; all networks were porous and similar

(b) E-P 730: solids ratios of 46.3 to 64.4%; very fine networks; the 64.4 solids ratio could not be dyed.

(c) AZO-77: solids ratios of 46.3 to 56.9%; the network had many large pores; the 56.9 ratio was the most dense with no discernable pores

(d) AZO-88: solids ratios of 46.3 to 64.4%; all networks had very fine pores; the 64.4 ratio was very difficult to dye.

No attempt has been made to compare networks of more than one grade of zinc oxide since reflectance is a function of particle size as well as of purity. Before any correlation is made between microstructure and reflectance it will be necessary to examine a series of coatings based on one grade of zinc oxide, using various particle sizes. These materials have been ordered, and extensive investigations will be made upon their receipt.

A zinc oxide-potassium silicate coating displayed a surprising increase in reflectance at 380 mμ from 30% to 60% after being "tumbled" in an Alconox-water mixture for 16 hrs. Thorough rinsing did not affect this increase; a 500°C heat treatment for 16 hrs also failed to lower the reflectance back to the characteristic 30 to 35% of silicate-bonded zinc oxide. X-ray studies using the powder pattern method revealed no phase other than zinc oxide; apparently the foreign component was either amorphous in extremely small quantities or of extremely fine crystallite size.

Experiments showed that both Alconox and aluminum are required to produce this optical change. Tumbling of a coating on Pyrex with Alconox-water did not change its reflectance. However, introduction of a small amount of aluminum dust into the tumbling system did result in upgrading of the near-ultraviolet reflectance. The necessity of Alconox was shown by the fact that substitution of a neutral organic wetting agent, "Tergitol," methanol, or dilute ammonium hydroxide failed to increase the ultraviolet reflectance. Figure 5 shows comparative reflectance
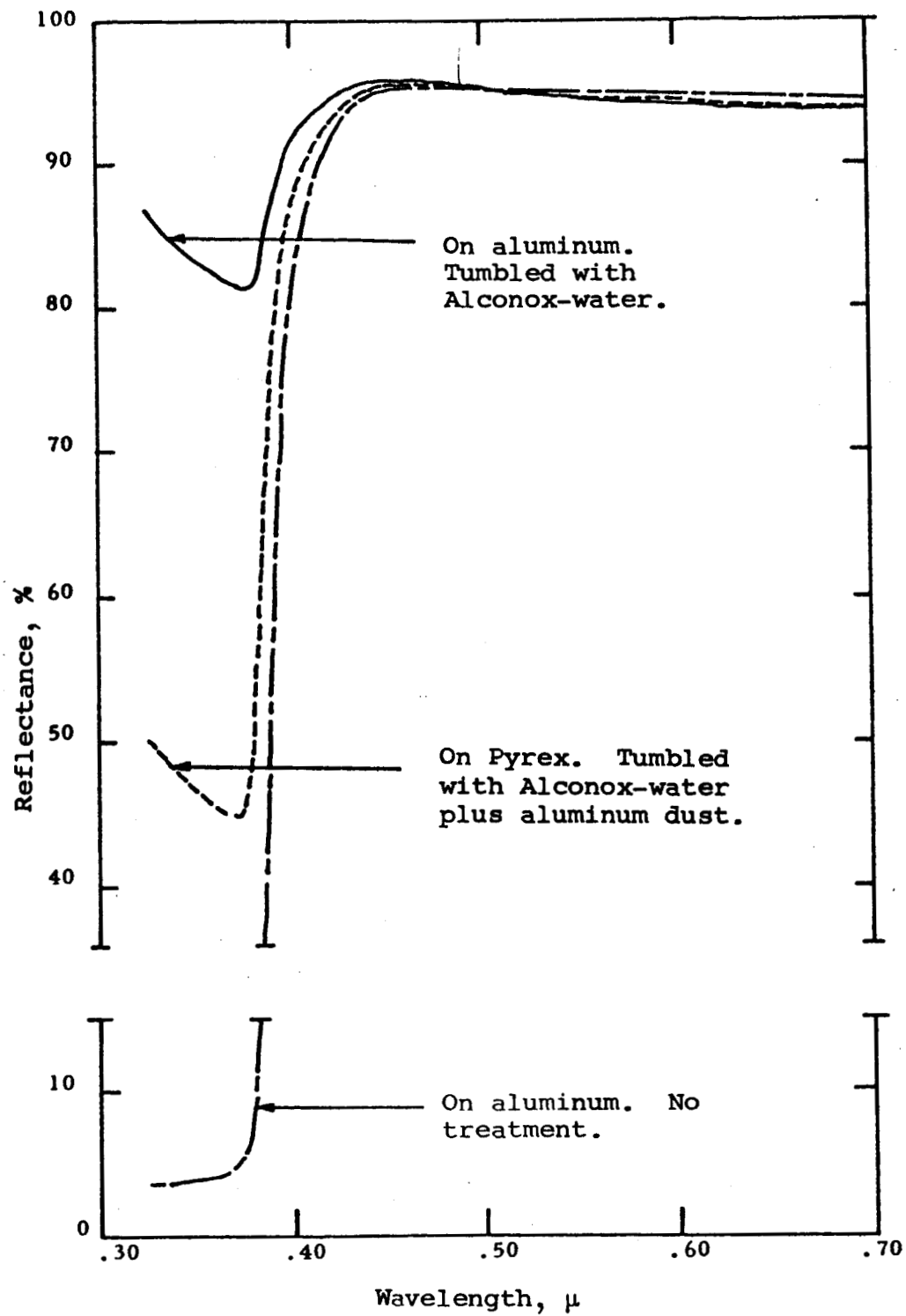
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Figure 5

REFLECTANCE AS A FUNCTION OF ALCONOX TREATMENT
FOR ZINC OXIDE-POTASSIUM SILICATE COATINGS

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curves for zinc oxide-potassium silicate coatings on Pyrex and aluminum which have been treated with Alconox; the sample on the aluminum substrate shows the best improvement.

Other tumbling media which did not yield improved reflectance on Pyrex-based coatings were Alconox-water plus a high purity fine alumina and aluminum leafing pigment incorporated with either Alconox-water or carbon tetrachloride. Allowing a sample on aluminum to merely be immersed in Alconox-water also did not affect the reflectance.

Attempts were made to improve the ultraviolet reflectance by incorporation of various additives in paint formulations. Small amounts each of Alconox, aluminum dust, and aluminum oxide were milled into zinc oxide-potassium silicate formulations. However, coatings of these compositions had reflectance curves identical to that of a paint without the additives.

Paint samples on aluminum which had received the detergent treatment were subjected to ultraviolet irradiation in vacuum in two tests, No.s 32 and 34. The exposure in Test 32 was for 87 hrs at 8.4 suns, or 730 ESH and in Test 34, 108 hrs at 8.9 suns, or 960 ESH. Vacuum level during both tests was maintained at 10^{-7} torr or higher.

Severe degradation occurred for all samples. Results are tabulated in Table 3.

In contrast to Hi-5-1, a standard untreated coating had a solar absorptance of .015 in Test 32. It is apparent that the component which upgraded the ultraviolet reflectance of

silicate-bonded zinc oxide is quite degradable. This component
may be the oxide, phosphate, or silicate of aluminum; these anions
all exist in the Alconox. Previous studies have revealed that
these aluminum compounds are quite degradable. Spectral reflectance
curves for sample HI-9-9 before and after ultraviolet irradiation
in vacuum appear in Figure 6.

Table 3

EFFECT OF ULTRAVIOLET IRRADIATION IN VACUUM
ON DETERGENT-TREATED ZINC OXIDE-POTASSIUM SILICATE COATINGS

| Sample | Test No. | Exposure (ESH) | Solar Absorptance | | | |
			α_1	α_2	α	$\Delta\alpha$
HI-5-1	32	0	.080	.063	.144	
		730	.286	.116	.402	.258
2WX	32	0	.083	.059	.142	
		730	.243	.085	.328	.186
HI-9-9	34	0	.042	.064	.107	
		960	.347	.131	.478	.371

The original solar absorptance values for the two samples
in Test 32 were higher than that of the sample in Test 34. This
was due to a more limited upgrading of the ultraviolet reflectance
for HI-5-1 and 2WX, and also to their lower reflectance values
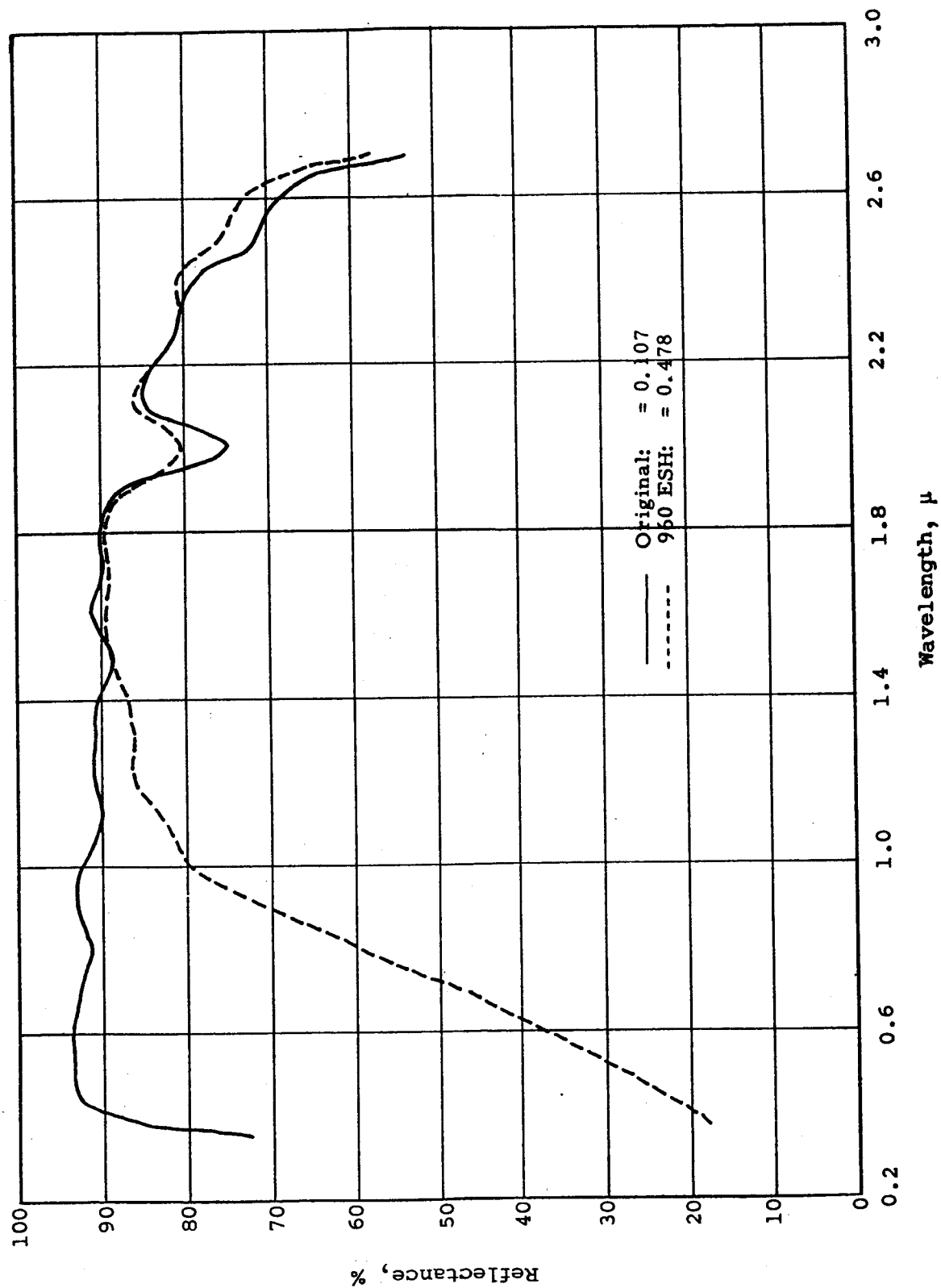in the visible spectrum since they were relatively thin, < 4 mils.

EFFECT OF 960 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE
OF DETERGENT-TREATED ZINC OXIDE-POTASSIUM SILICATE COATINGS

Figure 6

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IV. SILICONE COATINGS

A. Effect of Pigment Volume Concentration

SP 500 zinc oxide-pigmented methyl silicone (General Electric's LTV-602 elastomer) specimens were prepared with pigment volume concentrations (PVC) of 15, 20, 25, 30, 35, and 40%. The thickness of each film was 6.7 $\pm$ 0.1 mils; this was achieved by painting nearly 100 specimens and measuring the reflectance on those with thicknesses between 6.6 and 6.8 mils. The spectral reflectances of these films (applied to 6061 aluminum) were measured on a Cary integrating-sphere reflectometer in the wavelength range of 0.325 to 2.0μ.

The reflectance curves of five of the six films are presented in Figure 7. The curve for the paint pigmented at 30% PVC is not included because its refectance dropped below that of the coating with 25% PVC. The reason for this deviation is not known, but it could be due to either an error in formulation or soiling which occurred in its manufacture (the paints with different PVC's were manufactured separately rather than by "letting-down" a master batch pigmented at 40% PVC with LTV-602). A subsequent paint prepared at 30% PVC exhibited a reflectance curve between that of the 25% PVC paint and that of the 35% PVC paint. Because the specimen measured possessed a thickness slightly different from the other paints, it has not been included in Figure 7. The reflectance was measured against a magnesium carbonate block, and the curves presented in Figure 4 have not been adjusted to

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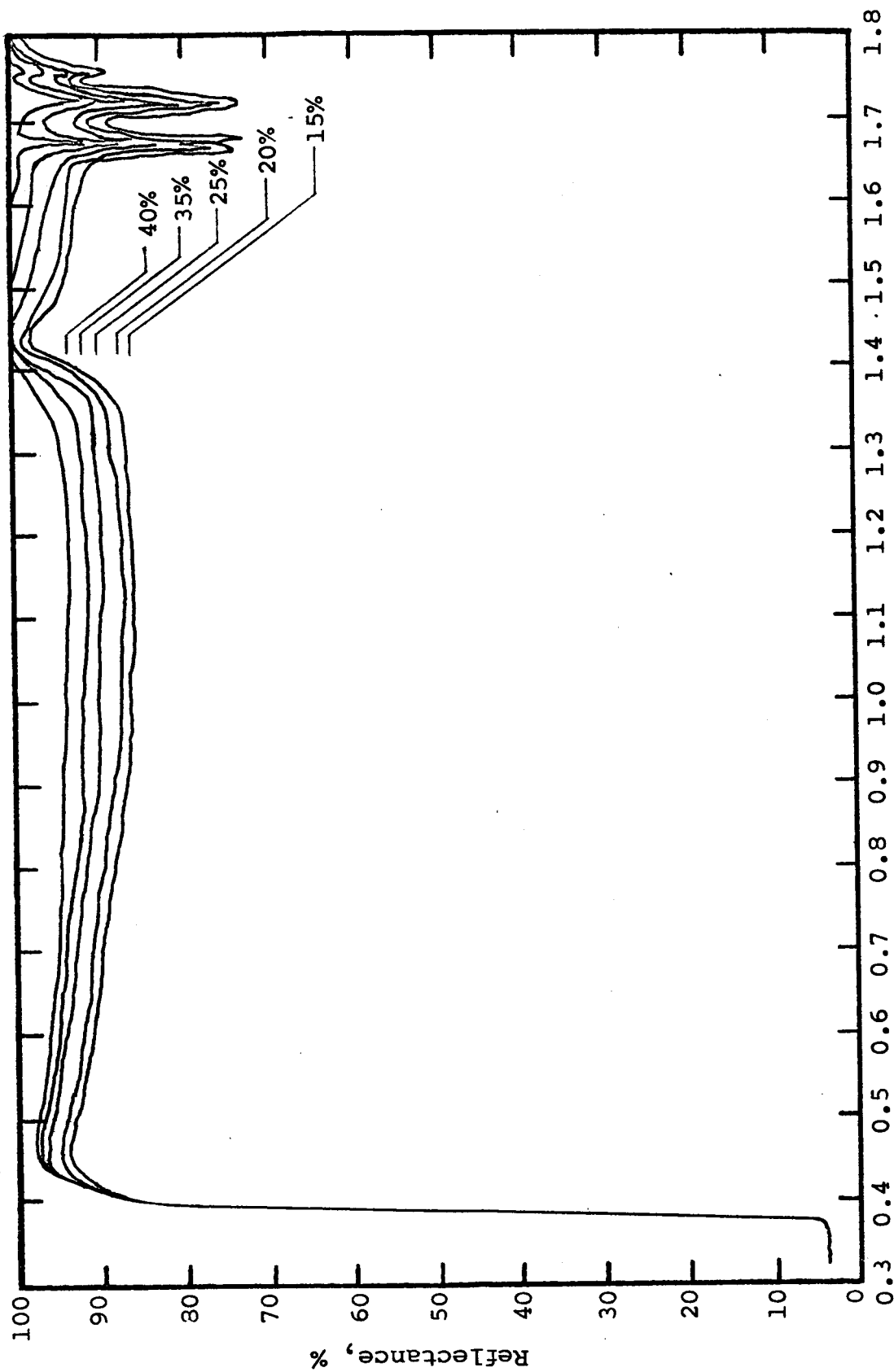
Wavelength, μ

Figure 7

SPECTRAL REFLECTANCE OF ZINC OXIDE-SILICONE PAINTS AT DIFFERENT PVCs
(Based on $MgCO_3$-Block)

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account for the absolute reflectance of magnesium carbonate. The reflectance peak at 1.43 μ wavelength is attributed to an absorption band in the carbonate block, and the 100% reflectance exhibited in this region by three of the paints is simply because the reflectance of the zinc oxide paints is greater than that of the magnesium carbonate standard. The absorption in the 1.7 μ region is attributed to the structure of the silicone vehicle and is somewhat masked at the highest pigment concentration.

These curves show the effect of increased particle-packing on the reflectance in the various regions of the spectrum. As the particles (mean diameter 0.3 μ) are packed more closely together, they tend to behave as a particle with a diameter larger than that of any single particle but smaller than the diameter of the aggregate. Thus, the packing of the particles appears to be manifested in the greater effect on the near-infrared reflectance of increased pigment concentrations. Still more work must be done to ascertain the true nature of these relationships. In this respect, the curves in Figure 4 provide a basis of comparison when varying other parameters such as particle size distributions; this will be attempted by blending different size zinc oxides which are available.

B. Effect of Multiple Coat Systems

The superior near-ultraviolet reflectance of tin oxide compared to zinc oxide suggested that it might be used in a

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very thin coating to upgrade the reflectance of paints based on zinc oxide. The spectral reflectance curves (compared to a magnesium oxide-smoked magnesium carbonate block) of USP tin oxide are given for a compact and for a paint in Figure 8. The paint was formulated from General Electric's SR-80 silicone resin (which closely approximates IITRI's experimental methyl-silicone resins except for ultraviolet stability) at 40% PVC. The visible spectral reflectance of the compact after receiving 1200 esh ultraviolet radiation in vacuum is also shown in Figure 8. The tin oxide paint was greatly diluted with toluene and spray-applied in a thin film to a 4-mil thick zinc oxide-methyl silicone paint. The zinc oxide paint was prepared from SP 500 zinc oxide and an experimental methyl-silicone resing at 40% PVC. The reflectances of the zinc oxide paint and that of the same paint oversprayed with the diluted tin oxide coating are shown in Figure 9.

Examination of Figures 8 and 9 show that although the tin oxide topcoat slightly upgraded the reflectance of the zinc oxide paint in the near ultraviolet, it had an adverse effect on the sprectral reflectance of the zinc oxide paint in the remainder of the spectrum. These results, coupled with the decrease in the reflectance of the tin oxide compact on irradiation, have resulted in discontinuation of the studies of tin oxide composites.

Current work involves a similar approach with materials such as the diatomaceous earths—both as topcoats and as part of the pigment system. Results thus far indicate that, unlike tin oxide composites, composites made from zinc oxide paints and a paint

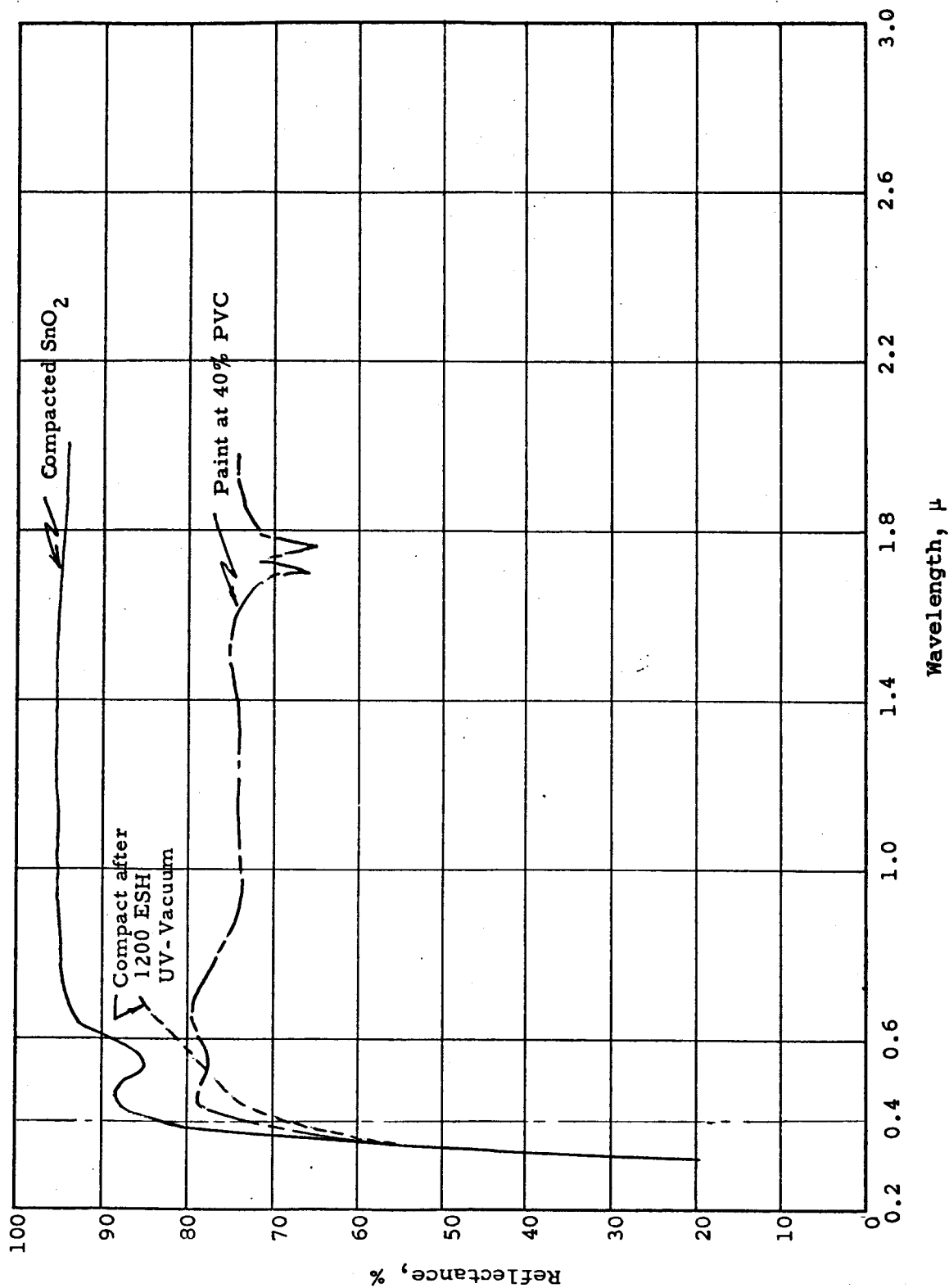SPECTRAL REFLECTANCE OF COMPACTED TIN OXIDE
AND TIN OXIDE-PIGMENTED SILICONE RESIN AT 40% PVC

Figure 8

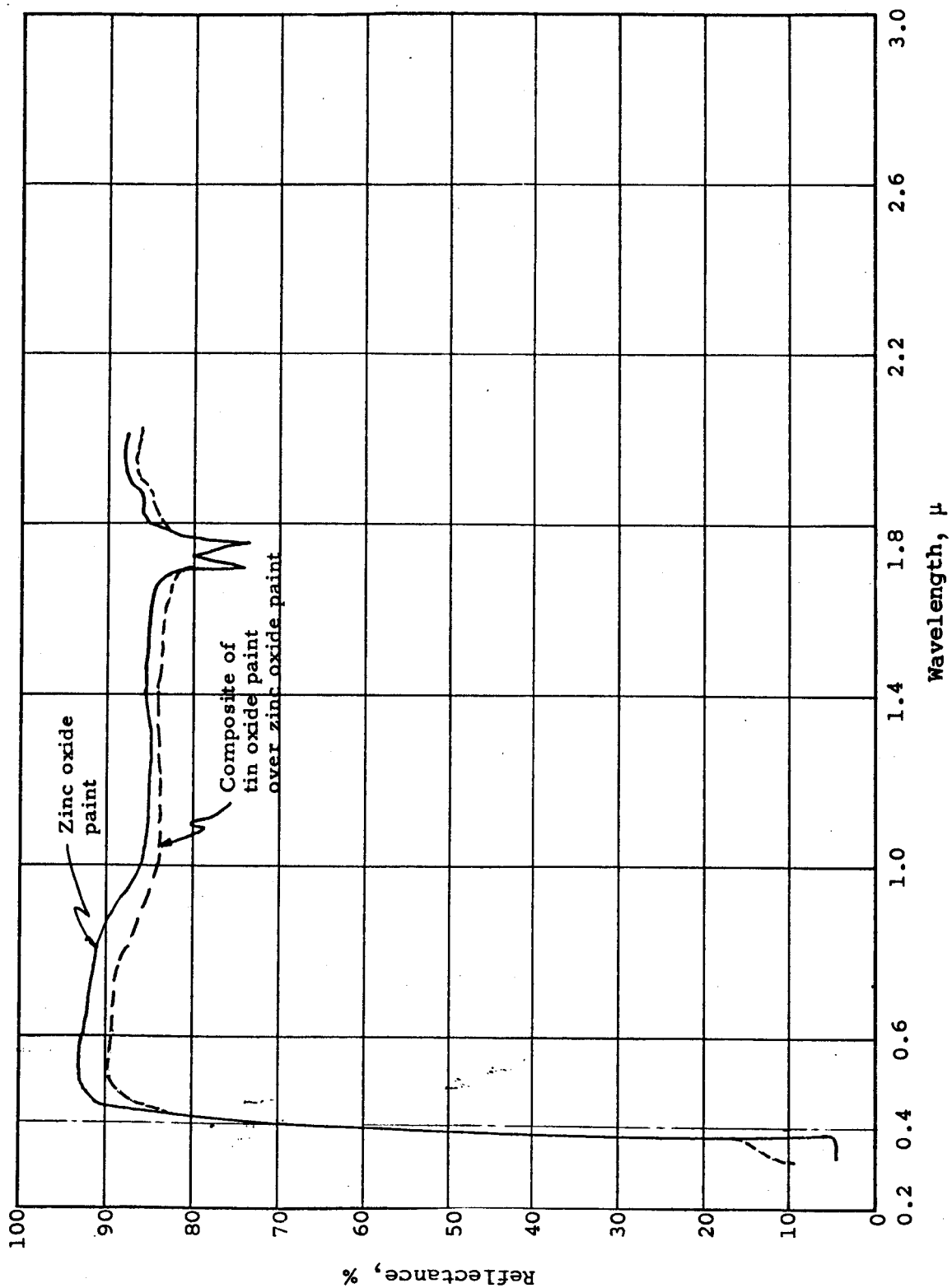32   IITRI-C6014-4

Figure 9

EFFECT OF SPRAYING A VERY THIN TOPCOAT OF A 40% PVC TIN OXIDE
PAINT ON A 40% PVC ZINC OXIDE PAINT

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pigmented with Dicalite WB5 (a diatomaceous earth) do not affect the reflectance in the visible and near-infrared region. Unfortunately, they do not serve to upgrade the reflectance of the zinc oxide paint in the ultraviolet. However, since these materials do not exhibit the visible and near-infrared absorption of tin oxide, more work will be done on them and on similar materials. In this respect, it is hoped that a diatomaceous silica can be obtained with a particle size such that ultraviolet scattering is enhanced.

V. MULTIFORM SILICA PAINT

The excellent reflectance reported for a multiform silica paint (Ref. 5) prompted us to obtain the material for ultraviolet tests. The reflectance of Corning Glass's 7941 multiform silica paint before and after exposure to 1200 ESH of ultraviolet-radiation in vacuum is presented in Figure 10. The solar absorptance before irradiation was 0.10. The reflectance was so decreased by 1200 ESH of irradiation at 10^{-7} torr that the solar absorptance after exposure was not computed.
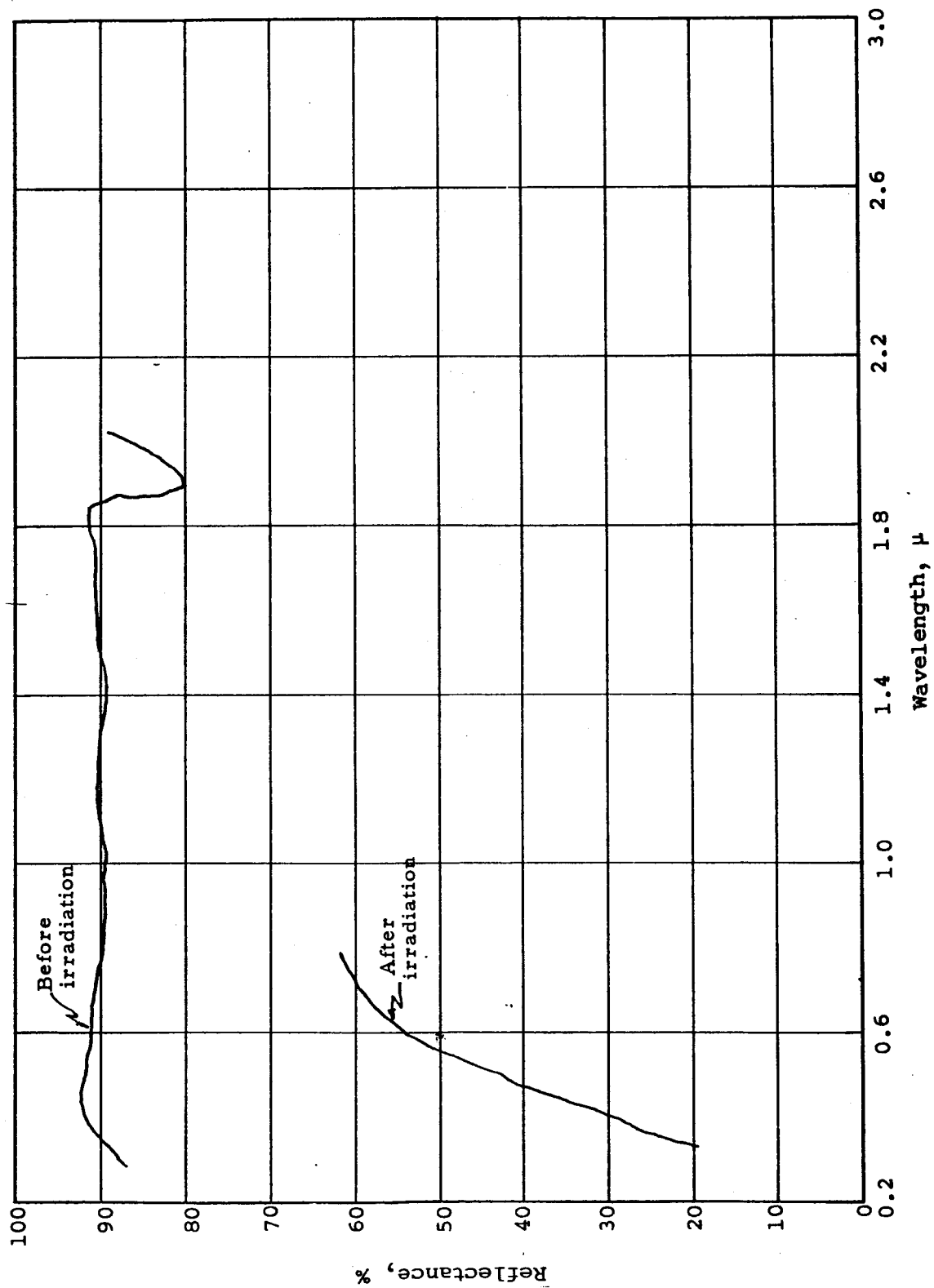
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Figure 10

EFFECTS OF 1200 ESH ULTRAVIOLET RADIATION IN VACUUM ON CORNING'S 7941 MULTIFORM SILICA PAINT

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VI. CONCLUSIONS AND FUTURE WORK

The studies on the creation of microporous structures in potential paint vehicles appear to be the most promising of the several approaches which have been initiated. Of immediate interest, therefore, is the effect on ultraviolet stability of the micropores designed to greatly increase the scatter of ultraviolet light. Although the results of the dual-coat systems have been somewhat disappointing, the difficulties incurred were not unexpected.

Most of our work directed toward microporosity in paint vehicles will be performed with the experimental R-5 methyl-silicone resin synthesized in our laboratories since it exhibits excellent ultraviolet stability. We will attempt to reduce the amount of TBT because this compound has a relatively poor ultraviolet stability. Attempts will also be made to obtain the desirable curing conditions by catalysis with zinc octoate or diethylenetriamine. Instead of methylene chloride, other low-boiling solvents will be tried. We plan to continue our efforts with the chemical blowing agents listed in Table 1; we will investigate these in combination with resin R-5.

Future work in the area of inorganic coatings will involve incorporation of other relatively stable pigments with zinc oxide. Not to be overlooked is the possible development of stable systems not employing zinc oxide. Application of a one-component zinc oxide coating by flame-spraying will also be investigated.

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We are planning additional studies on the importance of pigment particle-packing (e.g., PVC) for the silicone paints. Similarly, studies involving the microstructure of zinc oxide-potassium silicate coatings are currently in progress. Attempts will be made in the near future to increase the ultraviolet reflectance of zinc oxide paints by incorporation of porous, diatomaceous earth pigments into the paints as fillers.

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